THE BIMOLECULAR REDUCTION OF ALDEHYDES

BY

JOHN LEE MARSH

B.S., University of Rochester, 1938

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
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2,3-Dimethyl-1-naphthaldehyde was studied as a typical highly substituted aldehyde of the naphthalene series. Its bimolecular reduction by the binary mixture, Mg + MgI_2,[4] produced two isomeric glycols. The higher-melting of these, which is probably the meso isomer, was produced in the smaller amount. This may be due to the fact that the bulky aryl groups hinder the formation of the cyclic magnesium intermediate which yields this isomer.

2.3-Dimethyl-1-naphthaldehyde was prepared from 2,3-dimethylnaphthalene by the action of zinc cyanide, hydrogen chloride and aluminum chloride. Its name, guaialdehyde, is taken from that of the parent hydrocarbon, guaiene. The bimolecular reduction products of guaialdehyde were named the hydroguaioins. The isomers were differentiated in the customary way by applying the name isohydroguaioin to the lower-melting form.

The conversion of guaialdehyde to the known 1,2,3-trimethylnaphthalene [7] showed that the functional group occupies the 1-position. Aluminum isopropoxide converted guaialdehyde to the corresponding carbinol. Hydrogen peroxide, acting in refluxing acetic acid,[1] removed the functional group of guaialdehyde and produced 2,3-dimethyl-1,4-naphthoquinone, guaioquinone.[8] The glycol, isohydroguaioin, also yielded this quinone when treated in this manner. Alcoholic potassium hydroxide converted guaialdehyde to a highly insoluble white solid of undetermined structure.

In studying the coupling of benzaldehyde by the binary mixture, Mg + MgI_2, Gomberg and Bachmann [5] prepared the iodomagnesium salt of hydrobenzoin from methylmagnesium iodide and hydrobenzoin. Since the action of benzaldehyde on this salt yielded exactly the products formed in the bimolecular coupling (equation below), they concluded that such salts are intermediates in the coupling.

$$C_6H_5CHOMgICHOMgIC_6H_5 + C_6H_5CHO \rightarrow C_6H_5COCHOMgIC_6H_5 + C_6H_5CH_2OMgI$$

In this investigation mesitaldehyde was added to the same salt. No reaction occurred, for both mesitaldehyde and hydrobenzoin were recovered from the reaction mixture. Under like conditions isohydromesitoin was unaffected by benzaldehyde. These experiments indicate that di-ortho-substitution of either reactant is sufficient to prevent the reaction of a hydrobenzoinate and an aldehyde.

THE ALKYLATION OF PHENYLACETONITRILE

The methylation of phenylacetonitrile was studied during a search for a satisfactory synthesis of α-phenylpropionic acid. The enols derived from the α-methyldesoxybenzoins (I) were the final objective. The treatment of phenylacetonitrile with sodium amide and methyl sulfate [2] produced a mixture of the desired α-phenylpropionitrile with unchanged material and α-phenylisobutyronitrile, the dimethylated product. The latter by-product was produced in considerable amount even when methyl sulfate was used in amount stoichiometrically less than that required for monomethylation. Unchanged material was easily removed as its benzal derivative.

$$\begin{array}{l} \text{Ar-CO-CH-C}_6\text{H}_5 \\ \quad\quad\quad\

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VITA

The author was born in Washington, D. C., on February 25, 1916. The public schools of Niagara Falls, N. Y., were the scene of his elementary education. In 1938 he received the degree of Bachelor of Science at the University of Rochester. In the same year he entered the University of Illinois. There he has been a teaching assistant and a University fellow.

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